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A New Precursor of 1,3,4-Thiadiazole-sulfonamides: 5-*tert*-Butyloxycarbonylamino-1,3,4-thiadiazole-2-sulfonyl Chloride

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Abstract

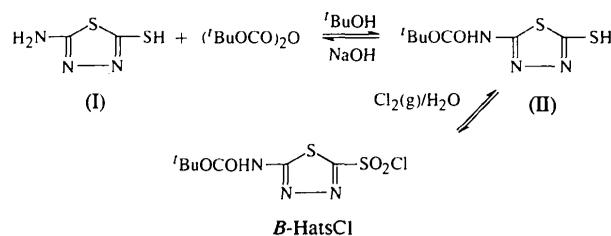
The title compound, *tert*-butyl 2-chlorosulfonyl-1,3,4-thiadiazole-5-carbamate, C₇H₁₀ClN₃O₄S₂, is a 1,3,4-thiadiazole derivative related to sulfonamides. Bond lengths and angles indicate a strong interaction between the sulfonyl group and the thiadiazole ring. The sulfonyl moiety presents a distorted arrangement around the S atom.

Comment

Since Davenport (1945) reported that thiophene-2-sulfonamide is 40 times more active as a carbonic anhydrase (CA) inhibitor than the sulfonamides, many

heterocyclic sulfonamides have been prepared. Two important facts connecting chemical structure with CA inhibitory action have been established. Firstly, five-membered derivatives are more effective than six-membered ones, and secondly, the presence of nitrogen and sulfur within the ring lead to the most potent CA inhibitors. We have obtained and determined the crystal structures of several 1,3,4-thiadiazolesulfonamides following the method proposed by Young, Wood, Eichler, Vaughan & Anderson (1956) with minor modifications (Alzuet, Ferrer & Borrás, 1991a; Pedregosa, Alzuet, Borrás, Fustero, García-Granda & Díaz, 1993).

In this work, as part of our program of systematic studies on unsubstituted sulfonamides and their metal complexes (Alzuet, Ferrer & Borrás, 1991b; Pedregosa, Casanova, Alzuet, Borrás, García-Granda & Gutierrez-Rodriguez, 1995), we have obtained and determined the crystal structure of 5-*tert*-butyloxycarbonylamino-1,3,4-thiadiazole-2-sulfonyl chloride (*B*-HatsCl) (*B* = butyloxycarbonyl), which is an intermediate in the synthesis of 5-*tert*-butyloxycarbonylamino-1,3,4-thiadiazole-2-sulfonamide (*B*-Hats) and 5-amino-1,3,4-thiadiazole-2-sulfonamide (Hats), in order to establish structural relations with sulfonamides. The presence of an S—Cl bond instead of the S—N bond in the structure may, however, provide an insight into the reactivity of the intermediate and coordination properties of these compounds.



The endocyclic bond length C(2)—N(2) [1.294 (4) Å] clearly indicates a double bond. The longer bond distances [C(1)—N(1) 1.317 (4) and C(1)—N(3) 1.354 (4) Å] can be explained by a slight delocalization of electron density through the N(1), C(1) and

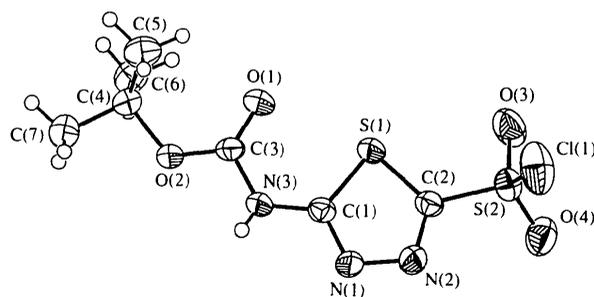
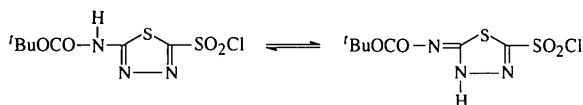


Fig. 1. The molecular structure of *B*-HatsCl showing the atom-numbering scheme and 50% probability displacement ellipsoids.

N(3) atoms (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), due to interaction between the thia-diazole ring and the substituted acetamido group, which leads to two possible tautomeric forms of the molecule.



It is noteworthy that in this structure we observe three different C—O bond distances. The C(3)—O(1) bond distance of 1.204(4) Å is characteristic of a double bond. The C(3)—O(2) distance of 1.319(4) Å, intermediate between that of a double and single bond, is shorter than the O(2)—C(4) length of 1.495(4) Å, which corresponds to a C—O single bond. This fact is related to the delocalization process involving the thia-diazole ring and the *tert*-butyloxycarbonylamino group. In fact, the C(3)—N(3) and N(3)—C(1) bond lengths are also intermediate between single and double bonds.

The S(2) atom, which lies in the ring plane, has a distorted tetrahedral environment. The significant widening of the O—S—O angle from the ideal tetrahedral value is the result of non-bonding interactions between short bonds (Cotton & Stokley, 1970).

Experimental

'BuOH/H₂O (1:1, 30 ml) and NaOH (0.6 g, 15 mmol) were added to 1.86 g of 5-amino-1,3,4-thiadiazole-2-thiol, (I), in an ice bath. ('BuOCO)₂O (3.27 g, 15 mmol) was added to the solution at room temperature with stirring. The resulting mixture was stirred for 14 h at room temperature and the excess ('BuOCO)₂O was extracted with ethyl acetate (25 ml). The aqueous layer was treated with aqueous KHSO₄ (2.5 g in 20 ml H₂O) and extracted with ethyl acetate (2 × 30 ml). After the usual workup and recrystallization, 2.44 g (75%) of (II) was isolated. 2.3g (10 mmol) of (II) in 200 ml of glacial acetic acid/H₂O (30:70) was chlorinated for 30 min at 278 K. The white precipitate obtained was removed by filtration, washed with cold water/hexane and dried in air. 2.60 g (89%) of *B*-HatsCl was obtained after recrystallization from Et₂O-1,2-dichloroethane (1:1).

Crystal data

C₇H₁₀ClN₃O₄S₂

M_r = 299.75

Monoclinic

*P*₂/c

a = 9.743(6) Å

b = 19.027(4) Å

c = 6.973(3) Å

β = 100.68(4)°

V = 1270(1) Å³

Z = 4

D_x = 1.57 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 15–18°

μ = 0.62 mm⁻¹

T = 293 K

Prismatic

0.23 × 0.23 × 0.16 mm

Colorless

Data collection

Enraf–Nonius CAD-4
diffractometer

ω/2θ scans

Absorption correction:

refined from Δ*F*

(*DIFABS*: Walker &
Stuart, 1983)

*T*_{min} = 0.65, *T*_{max} = 1.00

4290 measured reflections

1611 independent reflections

541 observed reflections

[*I* > 3σ(*I*)]

*R*_{int} = 0.027

θ_{max} = 25°

h = 0 → 11

k = 0 → 22

l = -8 → 8

3 standard reflections

monitored every 200

reflections

intensity decay: 3.00%

Refinement

Refinement on *F*

R = 0.036

wR = 0.036

S = 2.027

1343 reflections

194 parameters

Only H-atom *U*'s refined

w = 1/[σ²(*F_o*) + 0.0002*F_o*²]

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.24 e Å⁻³

Δρ_{min} = -0.26 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_j U_{ij} a_j^* a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S(1)	0.8826 (1)	0.14152 (5)	0.1190 (1)	0.0429 (3)
S(2)	1.0840 (1)	0.15032 (6)	-0.16181	0.0445 (3)
O(1)	0.6842 (3)	0.1496 (1)	0.3285 (4)	0.053 (1)
O(2)	0.6708 (3)	0.0810 (1)	0.5919 (3)	0.0398 (9)
O(3)	0.9697 (3)	0.1890 (2)	-0.2664 (4)	0.070 (1)
O(4)	1.1548 (3)	0.1009 (2)	-0.2574 (4)	0.062 (1)
N(1)	1.0358 (3)	0.0412 (2)	0.2875 (4)	0.040 (1)
N(2)	1.0986 (3)	0.0622 (2)	0.1371 (4)	0.042 (1)
N(3)	0.8414 (3)	0.0638 (2)	0.4293 (5)	0.038 (1)
C(1)	0.9216 (4)	0.0773 (2)	0.2945 (5)	0.034 (1)
C(2)	1.0288 (4)	0.1129 (2)	0.0406 (5)	0.037 (1)
C(3)	0.7247 (4)	0.1033 (2)	0.4428 (5)	0.037 (1)
C(4)	0.5429 (4)	0.1149 (2)	0.6397 (6)	0.041 (1)
C(5)	0.5749 (6)	0.1914 (2)	0.6930 (8)	0.053 (2)
C(6)	0.4216 (5)	0.1068 (3)	0.4695 (7)	0.053 (2)
C(7)	0.5198 (6)	0.0733 (3)	0.8155 (8)	0.057 (2)
Cl(1)	1.2277 (2)	0.21948 (7)	-0.0343 (2)	0.0834 (6)

Table 2. Selected geometric parameters (Å, °)

S(1)—C(1)	1.721 (3)	S(1)—C(2)	1.707 (4)
S(2)—O(3)	1.418 (3)	S(2)—O(4)	1.405 (3)
S(2)—C(2)	1.752 (4)	S(2)—Cl(1)	2.006 (2)
O(1)—C(3)	1.204 (4)	O(2)—C(3)	1.319 (4)
O(2)—C(4)	1.495 (4)	N(1)—N(2)	1.368 (4)
N(1)—C(1)	1.317 (4)	N(2)—C(2)	1.294 (4)
N(3)—C(1)	1.354 (4)	N(3)—C(3)	1.381 (5)
C(4)—C(5)	1.519 (6)	C(4)—C(6)	1.520 (6)
C(4)—C(7)	1.512 (6)		
C(2)—S(1)—C(1)	85.1 (2)	O(4)—S(2)—O(3)	120.7 (2)
C(2)—S(2)—O(3)	107.2 (2)	C(2)—S(2)—O(4)	111.1 (2)
Cl(1)—S(2)—O(3)	107.7 (2)	Cl(1)—S(2)—O(4)	106.6 (1)
Cl(1)—S(2)—C(2)	101.7 (1)	C(4)—O(2)—C(3)	120.4 (3)
C(1)—N(1)—N(2)	112.2 (3)	C(2)—N(2)—N(1)	110.5 (3)
C(3)—N(3)—C(1)	122.2 (3)	N(1)—C(1)—S(1)	114.9 (3)
N(3)—C(1)—S(1)	123.3 (3)	N(3)—C(1)—N(1)	121.8 (3)
S(2)—C(2)—S(1)	121.8 (2)	N(2)—C(2)—S(1)	117.4 (3)
N(2)—C(2)—S(2)	120.8 (3)	O(2)—C(3)—O(1)	128.9 (3)
N(3)—C(3)—O(1)	121.7 (3)	N(3)—C(3)—O(2)	109.3 (3)
C(5)—C(4)—O(2)	109.1 (3)	C(6)—C(4)—O(2)	110.0 (3)
C(6)—C(4)—C(5)	112.5 (4)	C(7)—C(4)—O(2)	102.1 (3)
C(7)—C(4)—C(5)	111.0 (4)	C(7)—C(4)—C(6)	111.6 (4)

The space group was determined to be $P2_1/c$ from the systematic absences. The data were measured using a variable scan rate with a maximum scan time of 60 s per reflection. The final drift correction factors were between 1.00 and 1.03. Profile analysis (Lehmann & Larsen, 1974; Grant & Gabe, 1978) was performed on all reflections. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985). Isotropic least-squares refinement using a local version of *SHELX76* (Sheldrick, 1976; van der Maelen Uría, 1990). Further anisotropic refinement followed by a difference Fourier synthesis allowed the location of all H atoms. During the final stages of the refinement the positional and anisotropic displacement parameters of the non-H atoms were refined. All H atoms were refined isotropically with individual displacement parameters. The function minimized was $\sum w(F_o - F_c)^2$. Geometrical calculations were carried out with *PARST* (Nardelli, 1983). All calculations were made at the University of Oviedo on the VAX computers of the Scientific Computer Center and X-ray group.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *DIRDIF* (Beurskens *et al.*, 1992). Data reduction: *DATAR*, local program. Molecular graphics: *EUCLID* (Spek, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,5-Bis(fluorodinitromethyl)-2-methoxy-1,3-dioxolane

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Abstract

The 1,3-dioxolane ring of the title compound, $C_6H_6F_2N_4O_{11}$, is in a slightly distorted 'twist' conformation. The largest deviations from the least-squares plane of the ring are exhibited by a C and an adjacent O atom which are displaced in opposite directions by about 0.23 Å. Bond distances agree well with those of the analogous formate ester, the major differences arising from the change in hybridization of the C5 atom from sp^2 in the ester to sp^3 in the present compound. The closest intermolecular interactions arise from nitro group O...O contacts of 2.9 Å between pairs of layers of molecules. Sublimed crystals 'jump' up to 1 cm and crack when gently heated (313 K).

Comment

The low-temperature structure determination of 4,5-bis-(fluorodinitromethyl)-2-methoxy-1,3-dioxolane, (I), was performed as part of a study of energetic materials containing the fluorodinitromethyl group. Details of the synthetic work have been discussed elsewhere (Koppes, 1995) and will be published separately (Koppes, 1996). The crystal structure of the analogous formate ester, 4,5-bis(fluorodinitromethyl)-1,3-dioxolan-2-one is known (Ammon & Bhattacharjee, 1984). In the ester, the ring conformation is determined by the planarity of the sp^2 -hybridized C5 atom with the three O atoms bound to it. The other two ring atoms, C1 and C3, are then displaced out of this plane in opposite directions by about 0.2 Å. In contrast, the 1,3-dioxolane ring in (I) has the C3 and O10 atoms displaced by 0.23 Å in